Light Induced Degradation in Manufacturable Multi-crystalline Silicon Solar Cells

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Abstract

Traditional Czochralski grown Si solar cells are known to suffer from light induced degradation (LID) which adversely affects the minority carrier lifetime. Multi-crystalline Si has also been shown to show a similar degradation/recovery cycle after a phosphorus gettering step. In this paper, promising ribbon and cast multi-crystalline Si are examined for light induced degradation. High oxygen materials ($\geq 10^{18} cm^{-3}$) like dendritic web, Baysix Cz, and conventional Cz show similar degradation/recovery, HEM cast multi-crystalline with modest oxygen content ($2.5x10^{17} cm^{-3}$) shows small LID, and EFG and string ribbon silicon with low oxygen content ($< 2.5x10^{17} cm^{-3}$) show no LID. In addition light induced degradation is investigated at elevated temperatures. It is shown that bulk lifetime is degraded at 400°C under tungsten halogen lamp illumination in a belt furnace suggesting that at 400°C LID is greater than any annealing. At higher temperature belt processing under lamp (>400°C) the net LID is partially reduced. On the other hand bulk lifetime is annealed in a conventional furnace at 400°C with no lamp illumination.

Introduction

Czochralski grown Silicon is known to suffer lifetime degradation and thus efficiency degradation under carrier injection. Light induced degradation (LID) was first studied by Fischer and Pschunder in 1973, after being recognized by Crabb in 1972 [1,2]. A great deal of attention has been directed at investigating ways to suppress or avoid LID especially since 1998 when Abe and Saitoh organized an international joint research focused on determining the cause of LID and how to avoid it in solar cell processing [3]. The trap formation has been shown to result from a boron-oxygen complex [4-7]. Various heat treatments have been implemented to improve the stabilized degraded lifetime of Cz wafers that suffer from LID [8]. Hydrogenation has also been shown to improve the stabilized degraded lifetime [8]. The effects of efficiency degradation can be reduced by wafer thinning, which improves the effective diffusion length ratio to device thickness to improve collection probability [9,10]. There is still much to be discovered about the trap responsible for LID. This paper analyzes the process conditions under which a sample will exhibit the degradation/recovery cycle in an industrial process. Different promising multi-crystalline Si materials with similar resistivity but varying oxygen content are analyzed for degradation along with the conditions under which degradation occurs for traditional high O_i content Cz Si.

Experimental

All materials listed in Table 1 received a light P diffusion of ~150Ω/sq. at 925°C and a 20nm oxide for passivation using the DOSS technique [11]. Then a 80nm SiN_x layer was deposited by PECVD at 300°C on top of the 20nm oxide to obtain a stack passivation.

This provided a stable surface passivation for ease of measurement and was monitored by a 2.3 Ωcm FZ wafer. Effective lifetime measurements were then made following light exposure and forming gas annealing at 400°C.

Table 1.

Material	Thickness	Resistivity	Oxygen (O_i)
Float Zone SEH	300 μm	2.3 Ωcm	undetected
Cz Baysix	400 μm	0.9 Ωcm	10^{17} to $2x10^{18}$
HEM	250 μm	1.5 Ωcm	$< 2.5x10^{17}$
Boron Web	102 μm	3.0 Ωcm	$> 1.0x10^{18}$
Magnetic Boron Web	93 μm	9.3 Ωcm	……
Gallium Web	97 μm	22.0 Ωcm	…….
Evergreen Ribbon	350 μm	3.0 Ωcm	$< 5.0x10^{16}$
EFG	350 μm	3.0 Ωcm	$< 4.0x10^{17}$

In addition, some additional Baysix Cz wafers were used to test degradation as a function of belt annealing (lamp illuminated heating) and furnace annealing (dark heating). The furnace anneal uses heating coils to achieve temperature allowing for samples to be heated essentially in the "dark". The belt furnace used in this study uses a bank of tungsten halogen lamps above and below samples to achieve the desired temperature. In all the experiments a very high lifetime (> 1ms) FZ (1.0 Ωcm) wafer was used for monitoring the change in surface passivation, if any, due to light exposure and/or annealing.

Results and Discussion

a.) Light Induced degradation in promising Multi-crystalline Si materials

After the light phosphorus diffusion samples were exposed to light for degradation and subsequently annealed in the tube furnace at 400°C for 15 minutes in Forming Gas for lifetime recovery. Figures 1-3 show the resulting effective lifetimes at $1x10^{15}cm^{-3}$

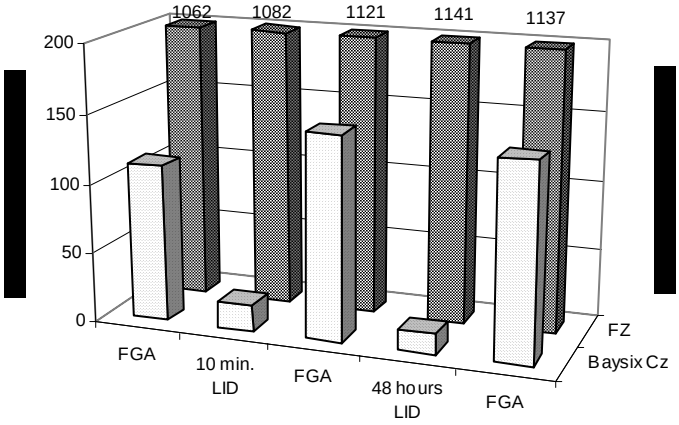

Figure 1. 2.3 Ωcm FZ and 0.9 Ωcm Baysix Cz under illumination and a 400°C forming gas anneal.

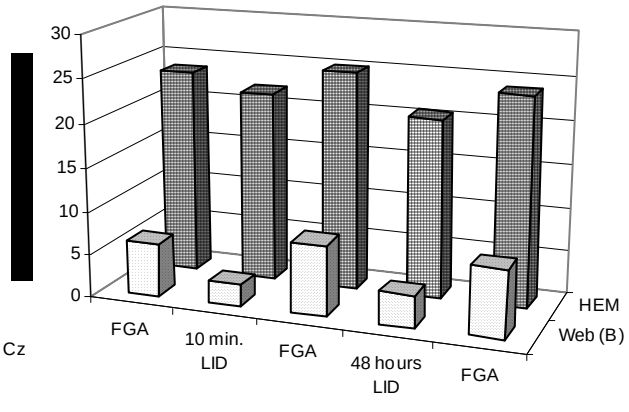

Figure 2. 1.5 Ωcm HEM and 3 Ωcm B Web under illumination and a 400°C forming gas anneal.

injection level for all the materials listed in Table 1. Effective lifetime

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s} \qquad (1)$$

which includes bulk lifetime (τ_b) and surface lifetime (τ_s). Figure 1 shows the effective lifetime for FZ and Cz Si. FZ maintains a stable effective lifetime of 1.2 ms and the Cz exhibits the traditional degradation recovery cycle. Figure 2 shows the degradation/recovery cycle for B doped dendritic web and HEM multi-crystalline Si. Figure 3 shows the low oxygen multi-crystalline Si ribbon materials EFG and String Ribbon that show no degradation. This information is consistent with the oxygen and boron data in Table 1, i.e., both oxygen and boron need to be present in sufficient amounts in order for degradation to occur. Fig. 2 demonstrates that even samples with lifetimes under 8μs can exhibit degradation. Figure 4 shows the normalized degradation for each material as function of the O_i content. The resistivity of each material is 1-3 Ωcm and is not considered in the figure. However, both single and multi-crystalline Si materials show an increase in normalized degradation with an increased oxygen concentration.

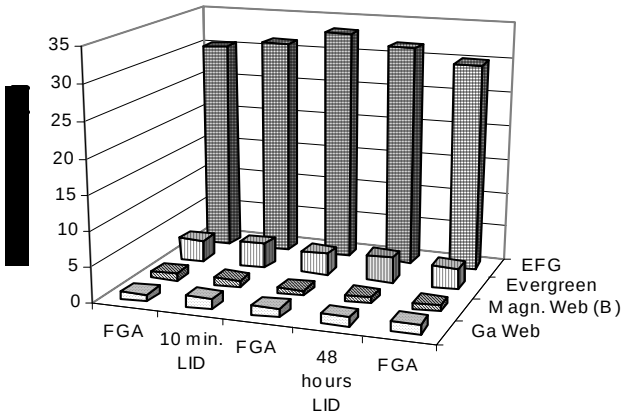

Figure 3. 3 Ωcm EFG, 3 Ωcm String Ribbon, 9.3 Ωcm magn.- B Web and 22 Ωcm Ga Web under illumination and a 400°C forming gas anneal.

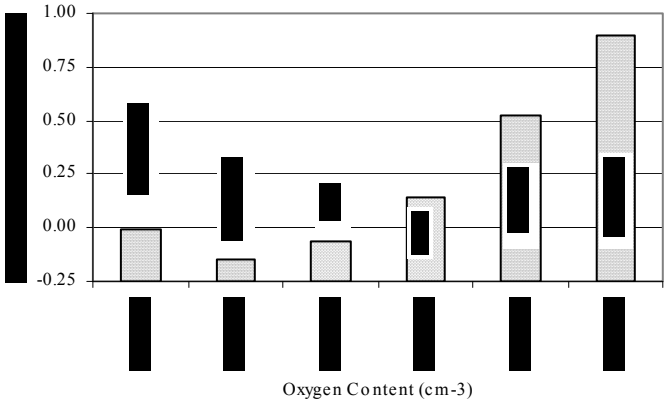

Figure 4. Normalized effective lifetime of manufacturable solar grade materials and there oxygen content

b.) Illuminated and Dark Annealing of LID

A study was conducted to compare illuminated annealing of LID in a belt furnace and dark annealing in a conventional tube furnace. In this study we examine degradation at elevated temperatures. It is commonly known that degradation occurs in the presence of light and that the lifetime is recovered by an anneal at 200°C and above. In an effort to further understand the trap responsible for LID, we performed a study comparing what happens to LID when light is used to heat the sample verses dark annealing. In the lamp heated belt furnace there may be a competition between degradation and recovery. In the conventional tube furnace we only have the recovery agent present. A high quality SiN_x / SiO_2 stack passivation was used to eliminate surface effects. This is supported by Figure

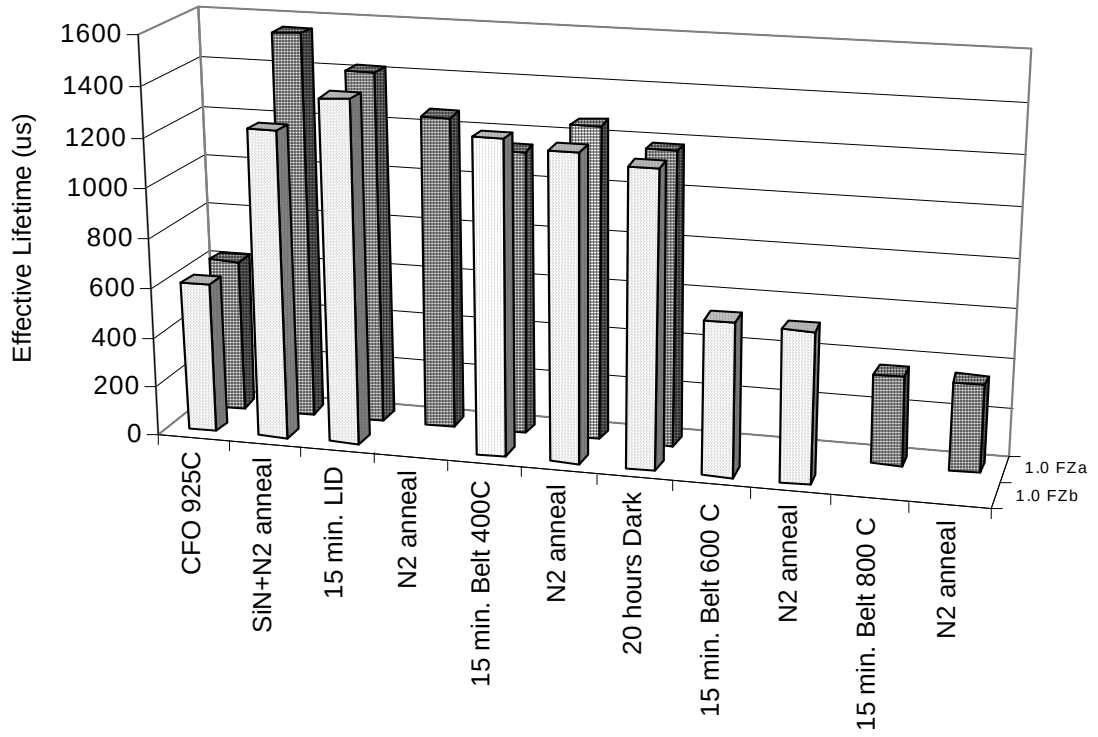

Figure 5. 1.0 Ωcm SEH FZ with a SiN_x / SiO_2 stack passivation. External stimulus applied is on the x-axis and measured effective lifetime is on the z-axis and the sample is on the y-axis. Bars on graph are in sequential order and therefore some x-axis labels do not apply for each sample.

5 which shows that effective lifetime for a 1.0 Ωcm SEH FZ wafer remains very high under various illumination and annealing conditions. The sample lifetime was measured immediately after a furnace oxide growth at 925°C and then a 80nm PECVD SiN_x layer deposited at 300°C. Following Nitride deposition the sample was annealed in N_2 at 400°C in a conventional furnace tube and re-measured. The samples were then degraded and annealed sequentially as shown Fig. 5. Surface passivation remains stable until the Belt furnace was raised to 600°C, the effective lifetime decreased to half the initial value and remained stable after additional N_2 anneal at 400°C. The surface passivation for FZ-b remained quite stable until the Belt furnace was raised to 800°C. The effective lifetime was then decreased to one-third the initial lifetime to 360μs and remained stable after additional N_2 anneal at 400°C. Thus surface passivation due SiN_x/SiO_2 stack remains sufficiently high to analyze PV grade materials by effective lifetime.

Figure 6a shows the effective lifetime of Baysix Cz samples subjected to the degradation/recovery sequence and the resulting effective lifetimes. The Cz samples show the expected cycle for the dark anneal at 400°C and 15 minutes or longer light soaking conditions. Results differ in Figure 6b when the LID Cz Si samples are subjected to illuminated heating/annealing. At 400°C under the tungsten halogen lamps in the belt furnace the samples show a similar degradation to 15 minutes light soaking in open air by a 300 W halogen lamp at 6 inch spacing. Cz samples that were degraded to 35μs showed no recovery in the illuminated belt furnace at 400°C. The effective lifetime is completely recovered in all Cz samples subjected to a 400°C belt anneal after a

subsequent N_2 anneal at 400°C in the dark. Figure 6b shows that there is LID during

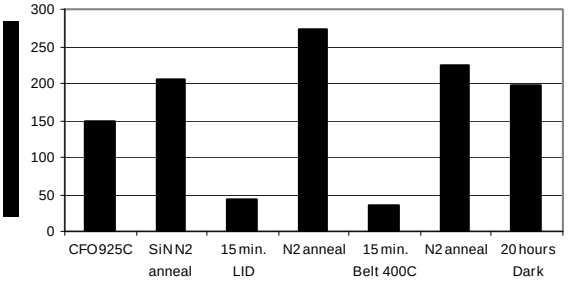

Figure 6a. 0.9 Ωcm Baysix Cz with a SiN_x / SiO_2 stack passivation. External stimulus applied is on the x-axis and measured effective lifetime is on the y-axis.

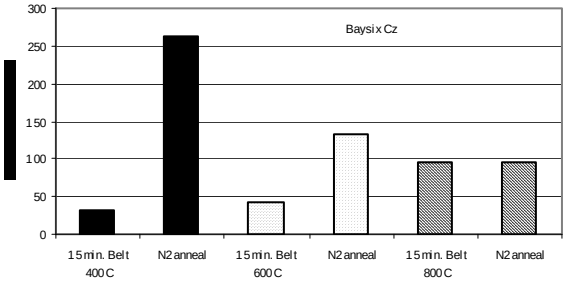

Figure 6b. 0.9 Ωcm Baysix Cz with a SiN_x / SiO_2 stack passivation. External stimulus applied is on the x-axis after N_2 anneal and measured effective lifetime is on the y-axis.

processing in the lamp heated belt furnace and the net LID is lower for higher temperature processing. Effective lifetime after 400°C heat treatment in the belt is about 1/3 the effective of lifetime of the 800°C anneal. After N_2 anneal the sample processed at 400°C fully recovers, while the effective lifetimes in 600°C and 800°C processed samples do not fully recover, possibly due to the decrease in surface passivation shown by the FZ wafers. However the 600°C sample recovers 90μs of effective lifetime due to the subsequent dark N_2 anneal, suggesting that LID remained after the 600°C process. On the other hand the 800°C showed no lifetime recovery after the subsequent dark anneal, suggesting that degradation and recovery is masked by the surface passivation. Partial recovery in these samples may be due to cooling in the dark after the sample exits the illuminated zone.

Conclusion

Light induced degradation in promising solar grade materials has been shown to occur in samples that have sufficient amount of boron and oxygen present for degradation. Both in single and multi-crystalline Si LID is proportional to the oxygen content. Cz and web Si show higher LID, HEM multi-crystalline Si shows some LID, and low oxygen Si ribbons show no LID. These results are consistent with the fact that LID is controlled by the oxygen and boron concentration and not by crystal defects and structure. In addition, light induced lifetime degradation is shown to occur at elevated temperatures during the processing in a lamp heated belt furnace. Degree of degradation is a function of the processing temperature.

Acknowledgements

This work was supported by Sandia National Laboratories contract #AO-6062 and NREL contract #XAF8-17607-05.

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